

# Symbolic Algebra in Functional Derivative Potential Calculations

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**ABSTRACT:** This article gives the details of the methodology used in constructing a symbolic algebra program designed for evaluating potentials as the functional derivatives of so-called functional generators in molecular density-functional theory. The derived formulae are used in illustrative examples involving partial functional integration, the comparison of the exchange potential arising from different mathematical representations of the electron density for a given functional generator, and the evaluation and comparison of the potential for different functional generators with a given density. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 300–307, 1998

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## Methodology

This article utilizes the previously published *Mathematica*<sup>1</sup> symbolic functional derivative calculation protocol in illustrative examples drawn from density functional theory.<sup>2</sup>

Consider first the general density functional formulation for the total electronic exchange energy. (The extension to other energy functional genera-

tors is straightforward.) This is usually written as an integral over real space,

$$E_x[\rho(\mathbf{r})] = \int d^3\mathbf{r} \rho(\mathbf{r})^{4/3} g_x(\mathbf{r}). \quad (1)$$

In the local density approximation to the electronic energy, based on considerations of the uniform electron gas, the functional generator  $g_x(\mathbf{r})$  is a constant.<sup>3</sup> In more realistic descriptions of atoms and molecules, the effects of inhomogeneities in the electron density are explicitly introduced into the exchange energy expression by allowing  $g_x(\mathbf{r})$  to depend on the density  $\rho$ , its gradient  $\nabla\rho$  (as in the work of Becke<sup>4</sup>), and higher derivatives such as  $\nabla^2\rho$  (as in refs. 5 and 6).

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In addition to determining the total energy, the density functional determines the forms of atomic and molecular orbitals, through the operation of the variational principle, that is, through the Kohn-Sham equations.<sup>7</sup> Each term in the functional gives rise to an effective potential experienced by the orbitals from which the density is built. The potentials are constructed from the functionals as their functional derivatives, for example, for the exchange potential,  $v_x(\mathbf{r})$ ,

$$v_x(\mathbf{r}) = \frac{\delta E_x[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}. \quad (2)$$

In this case, a simple relationship does not exist between the initial functional generator and the form of the potential, as in the exact case of hydrogen for which the exchange potential is

$$v_K^H(r) = e^{-2r} \left( 1 + \frac{1}{r} \right) - \frac{1}{r}. \quad (3)$$

For complex functional generators, which give reasonable approximations to the energy, it soon becomes difficult to obtain the corresponding potentials “by hand.”

## FUNCTIONAL DERIVATIVES

Let us consider the manual calculation of a potential as would be used in density functional theory. An example of such a general functional would be

$$F[\rho(\mathbf{r})] = \int d^3\mathbf{r} f[\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r})]. \quad (4)$$

The exchange potential is obtained as the functional derivative of the exchange energy, using the calculus of variations,<sup>3,8</sup>

$$\frac{\delta F[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} = \frac{\partial f}{\partial \rho} - \nabla \cdot \left( \frac{\partial f}{\partial \nabla \rho} \right) + \nabla^2 \left( \frac{\partial f}{\partial \nabla^2 \rho} \right). \quad (5)$$

For example, consider the functional  $F[\rho(\mathbf{r})]$ , defined as,

$$F[\rho(\mathbf{r})] = \int d^3\mathbf{r} \left[ \frac{\nabla^2 \rho(\mathbf{r})}{\rho(\mathbf{r})^{1/3}} \right]. \quad (6)$$

Through the simple application of eq. (5), one readily obtains the functional derivative,

$$\frac{\delta F[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} = \frac{4|\nabla\rho(\mathbf{r})|^2}{9\rho(\mathbf{r})^{7/3}} - \frac{2\nabla^2\rho(\mathbf{r})}{3\rho(\mathbf{r})^{4/3}}. \quad (7)$$

For more complicated functionals, however, this

manual procedure soon becomes unwieldy. For this reason, we generated automatic symbolic techniques for the evaluation of  $\delta F/\delta \rho$ . These techniques are implemented in the symbolic algebra system of *Mathematica*,<sup>1</sup> and have been made available to the scientific community.<sup>2</sup> In this article we describe the operation of the techniques, and give illustrations of their use.

We first introduce tensor suffix notation, including a summation convention for repeated indices, for the derivatives of the density:

$$\rho_i = \frac{\partial \rho}{\partial r_i}, \quad (8)$$

$$\rho_{ij} = \frac{\partial^2 \rho}{\partial r_i \partial r_j}. \quad (9)$$

Thus, for example, the Laplacian  $\nabla^2 \rho$  is written as  $\rho_{ii}$ , and  $\nabla_i(\nabla^2 \rho)$  as  $\rho_{ijj}$ .

For a large class of functionals, it is possible and convenient to express the functional integrand  $f(\rho, \nabla\rho, \nabla^2\rho)$  in terms of  $\rho$  and the two dimensionless parameters  $x(\rho, |\nabla\rho|)$  and  $y(\rho, |\nabla\rho|, \nabla^2\rho)$ , defined as,

$$x = \frac{|\nabla\rho|}{\rho^{4/3}} = (\rho_i \rho_i)^{1/2} \rho^{-4/3}, \quad (10)$$

$$y = \rho^{-(5/3)} \left[ \frac{\rho_i \rho_i}{\rho} - \rho_{ii} \right] = x^2 - \rho^{-(5/3)} \nabla^2 \rho, \quad (11)$$

where  $x$  is the dimensionless scalar density gradient, and  $y$  is a convenient dimensionless formulation of the Laplacian of the density. Note that in this application it is expedient to expand the gradient of the density explicitly as  $|\nabla\rho| = (\rho_i \rho_i)^{1/2}$ .

We examine the automatic functional differentiation of such functionals in the remainder of this article; more general functionals can be treated using exactly the same techniques, but these functionals serve as a good illustrative example.

## SYMBOLIC CALCULATION

A typical exchange-correlation (xc) energy density functional is given by

$$E_{xc}[\rho(\mathbf{r})] = \int d^3\mathbf{r} \rho(\mathbf{r})^{4/3} g(x(\mathbf{r}), y(\mathbf{r})). \quad (12)$$

For example, such functionals have been explored as candidates for improved representation of ex-

change in asymptotic regions far from the nuclei of a molecule.<sup>5</sup>

The functional derivative given by eq. (5) can be written as

$$v_{xc} = v_0 - v_1 + v_2, \tag{13}$$

where the terms are calculated by chain-rule differentiation as follows.

The first term is the straightforward partial derivative of the functional with respect to the density,

$$v_0 = \frac{\partial f}{\partial \rho}. \tag{14}$$

The second term is the divergence of the partial derivative of the functional with respect to the gradient of the density,

$$v_1 = \nabla_i \frac{\partial f}{\partial \rho_i}. \tag{15}$$

This is rather more complex than the previous term, because the functional is assumed to depend on the *modulus* of the gradient; therefore, an application of the chain rule is required,

$$v_1 = \frac{\partial}{\partial r_i} \left[ \frac{\partial f}{\partial |\nabla \rho|} \frac{\partial |\nabla \rho|}{\partial \rho_i} \right]. \tag{16}$$

This is expanded to give the result

$$v_1 = \frac{\rho_{ii}}{|\nabla \rho|} \frac{\partial f}{\partial |\nabla \rho|} + \frac{\rho_i}{|\nabla \rho|} \frac{\partial}{\partial r_i} \left[ \frac{\partial f}{\partial |\nabla \rho|} \right] - \frac{\rho_i}{|\nabla \rho|^2} \frac{\partial f}{\partial |\nabla \rho|} \frac{\partial |\nabla \rho|}{\partial r_i}, \tag{17}$$

which is then developed further using automatic symbolic manipulation, expanding all derivatives in terms of the spatial derivatives of  $\rho$ , and the derivatives of  $f$  or  $g$  with respect to  $|\nabla \rho|$  or  $x$  as desired.

The final term is the Laplacian of the partial derivative of the functional generator with respect to the Laplacian of the density, and this is developed in exactly the same way towards an expression involving derivatives of  $f$  or  $g$  with respect to  $x$  and  $y$ ,

$$v_2 = \frac{\partial}{\partial r_i} \left[ \frac{\partial}{\partial r_i} \left[ \frac{\partial f}{\partial \rho_{jj}} \right] \right]. \tag{18}$$

Examples of Functional Derivative Calculations

TWO-PARAMETER FUNCTIONAL GENERATOR

For a general, two-parameter functional generator  $g(x, y)$  for use in (12), which introduces the density, its gradient, and the Laplacian of the density, the potential given by eq. (2), takes the form,

$$v = \rho^{1/3} \sum_{m,n=0}^3 A_{mn} \frac{\partial^{(m+n)} g}{\partial x^m \partial y^n}, \quad m+n \leq 3, \tag{19}$$

where the coefficients,  $A_{mn}$ , are defined in Table I.

For the special case of an exponential density,  $\rho = N \exp(-ar)$ , this may be analyzed entirely in terms of  $x$  and  $y$  after eliminating  $N$  and  $a$ :

$$v = \rho^{1/3} \sum_{m,n=0}^3 B_{mn} \frac{\partial^{(m+n)} g}{\partial x^m \partial y^n}, \quad m+n \leq 3, \tag{20}$$

TABLE I. General Coefficients in Eq. (19).

<i>m</i>	<i>n</i>	<i>A<sub>mn</sub></i>
0	0	$\frac{4}{3}$
		$\frac{4x^2}{9}$
		$8\rho_i\rho_{ij}\rho_j + \rho_{ijj}$
0	1	$-4\rho_{ij}\rho_j - 3x^4 - 2\rho_{ij}^2 - \frac{14x^2y}{9} - \frac{5y^2}{3}$
0	2	$x^6 + 4x^2\rho_i\rho_{ij}\rho_j + 2x^2\rho_{ijj}\rho_j + 4\rho_i\rho_{ij}\rho_{jkk}$
		$+ \frac{20y\rho_i\rho_{ij}\rho_j}{3} + \frac{10y\rho_{ijj}\rho_j}{3}$
		$-4\rho_i\rho_{ij}\rho_{jk}\rho_k - \rho_{ijj}\rho_{ikk} - \frac{25x^2y^2}{9} - \frac{10x^4y}{3}$
1	0	$\frac{\rho_i\rho_{ij}\rho_j}{x^3} + \frac{y}{x} - \frac{7x}{3}$
1	1	$x^3 + \frac{xy}{3} + \frac{\rho_i\rho_{ij}\rho_{jk}\rho_k}{x^3} - \frac{2\rho_i\rho_{ij}\rho_j}{3x} - \frac{\rho_{ij}^2}{x}$
1	2	$\frac{22x\rho_i\rho_{ij}\rho_j}{3} + \frac{10y\rho_i\rho_{ij}\rho_j}{3x} + \frac{2\rho_i\rho_{ij}\rho_{jkk}}{x}$
		$-\frac{8x^5}{3} - \frac{40x^3y}{9} - \frac{4\rho_i\rho_{ij}\rho_{jk}\rho_k}{x} - \frac{8x\rho_{ij}\rho_j}{3}$
		$\frac{4x^2}{3} - \frac{\rho_i\rho_{ij}\rho_j}{x^2}$
2	0	$\frac{8\rho_i\rho_{ij}\rho_j}{3} - \frac{16x^4}{9} - \frac{\rho_i\rho_{ij}\rho_{jk}\rho_k}{x^2}$
2	1	

**TABLE II.**  
Coefficients in Eq. (20) for Exponential Density.

$m$	$n$	$B_{mn}$
0	0	$\frac{4}{3}$
0	1	$-\frac{4x^2}{9}$
0	2	$\frac{4x^2y}{9} - \frac{2y^2}{3}$
0	3	$\frac{2y^3}{3} - \frac{4x^2y^2}{9} - \frac{y^4}{4x^2}$
1	0	$\frac{y}{x} - \frac{4x}{3}$
1	1	$\frac{x^3}{3} + \frac{xy}{3} - \frac{y^2}{2x}$
1	2	$\frac{xy^2}{3} - \frac{4x^3y}{9}$
2	0	$\frac{x^2}{3}$
2	1	$-\frac{x^4}{9}$

where the coefficients,  $B_{mn}$ , are defined in Table II. This approach can be helpful in searching for universal energy functionals having the same properties for all densities of a given shape but different scaling. Similarly, for a Gaussian density,  $\rho = M \exp(-br^2)$ , one obtains the potential,

$$v = \rho^{1/3} \sum_{m,n=0}^3 C_{mn} \frac{\partial^{(m+n)} g}{\partial x^m \partial y^n}, \quad m+n \leq 3, \quad (21)$$

where the coefficients,  $C_{mn}$ , are defined in Table III.

### EXPLICIT FUNCTIONAL GENERATORS

The general expression, eq. (19), can be tested by evaluating the functional derivatives of the functional generators  $g_1 = \rho^{-(5/3)} \nabla^2 \rho = x^2 - y$ , and  $g_2 = \rho^{-(8/3)} |\nabla \rho|^2 = x^2$ ; that is,

$$E_1 = \int d^3\mathbf{r} \rho^{4/3} \left[ \frac{\nabla^2 \rho}{\rho^{5/3}} \right] = \int d^3\mathbf{r} \left[ \frac{\nabla^2 \rho}{\rho^{1/3}} \right], \quad (22)$$

$$E_2 = \int d^3\mathbf{r} \rho^{4/3} \left[ \frac{|\nabla \rho|^2}{\rho^{4/3}} \right]^2 = \int d^3\mathbf{r} \left[ \frac{|\nabla \rho|^2}{\rho^{4/3}} \right]. \quad (23)$$

**TABLE III.**  
Coefficients in Eq. (21) for Gaussian Density.

$m$	$n$	$C_{mn}$
0	0	$\frac{4}{3}$
0	1	$-\frac{4x^2}{9}$
0	2	$\frac{4x^2y}{9} - \frac{2y^2}{3}$
0	3	$-\frac{4x^2y^2}{9}$
1	0	$\frac{2y}{3x} - \frac{4x}{3}$
1	1	$\frac{x^3}{3} + \frac{5xy}{9} - \frac{2y^2}{9x}$
1	2	$-\frac{4xy^2}{9} - \frac{4x^3y}{9}$
2	0	$\frac{x^2}{3} + \frac{y}{3}$
2	1	$-\frac{x^4}{9} - \frac{2x^2y}{9} - \frac{y^2}{9}$

These are correctly evaluated and the values of the potential arising from each are

$$v_1 = \frac{1}{3} v_2 = \frac{4|\nabla \rho|^2}{9\rho^{7/3}} - \frac{2\nabla^2 \rho}{3\rho^{4/3}} = \frac{2}{3} \left( y - \frac{1}{3} x^2 \right) \rho^{1/3}, \quad (24)$$

as is to be expected from partial integration of eq. (22). It should be noted that eq. (24) can be rewritten in the form

$$v_1 = \frac{2}{3} \rho^{1/3} \left( 2g_1 - \frac{5}{6} x \frac{\partial g_1}{\partial x} - y \frac{\partial g_1}{\partial y} \right) \\ = \rho^{1/3} \sum_{ij=0}^1 A_{ij} \frac{\partial^{(i+j)} g_1}{\partial x^i \partial y^j}, \quad i+j \leq 1, \quad (25)$$

where the coefficients are,  $A_{00} = 4/3$ ,  $A_{10} = -5x/9$ , and  $A_{11} = -2y/3$ . Equation (25) is a specific case of the general form of the exchange potential given above.

### ONE-PARAMETER FUNCTIONAL GENERATOR

One can now simplify the analysis by using the symbolic computational methods described above to generate the potential given by eq. (2) for a

general functional generator,  $g(x)$  of  $x$  alone,

$$v = \rho^{1/3} \sum_{m=0}^2 D_m \frac{d^m g}{dx^m}, \tag{26}$$

where the coefficients  $D_m$  are defined in Table IV.

The same potential, with an exponential density  $\rho = N \exp(-ar)$ , explicitly introduced is given by

$$v_x = \frac{4a}{3x} g(x) + 2a \left( \frac{1}{ar} - \frac{2}{3} \right) g'(x) + \frac{ax}{3} g''(x). \tag{27}$$

The formulation of this exchange potential for a hydrogenic density with  $a = 2$  is confirmed in the work of Gill and Pople.<sup>9</sup>

Utilizing the Derived Potentials

EFFECTS OF DENSITY APPROXIMATION

To investigate the computational method, the exchange potential using the Becke functional generator<sup>4</sup> was computed analytically for STO-2G, STO-3G, and STO-6G approximations to an expo-

TABLE IV.  
Coefficients in Eq. (26).

<i>m</i>	<i>D<sub>m</sub></i>
0	$\frac{4}{3}$
1	$\frac{\rho_i \rho_{ij} \rho_j}{x^3} - \frac{4x}{3} - \frac{\rho_{ij}}{x}$
2	$\frac{4x^2}{3} - \frac{\rho_i \rho_{ij} \rho_j}{x^2}$

nential density arising from a wave function with  $a = 2$ . The differences in each case were found to be small, and the difference between the exact potential and that involving the Gaussian approximations to it are shown in Figures 1 and 2. In all cases, a shell-like structure is displayed at radial distances of up to 1.5 bohr from the nucleus; at distances greater than about 4 bohr, the difference in potential between the exact density and the Gaussian approximations tends to zero for STO-3G, and to small residual positive and negative values for STO-6G and STO-2G, respectively.

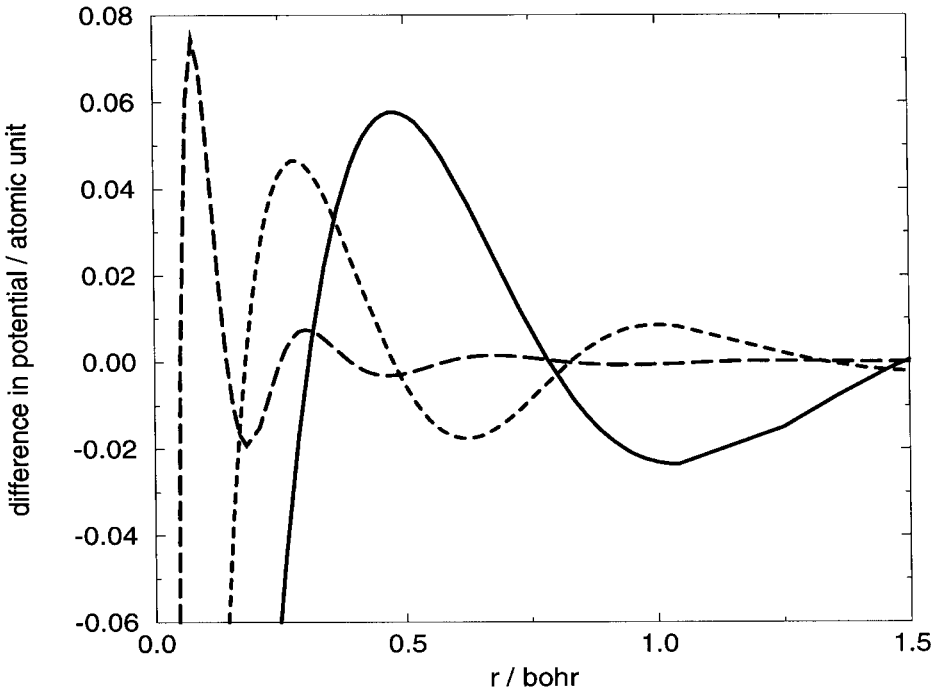
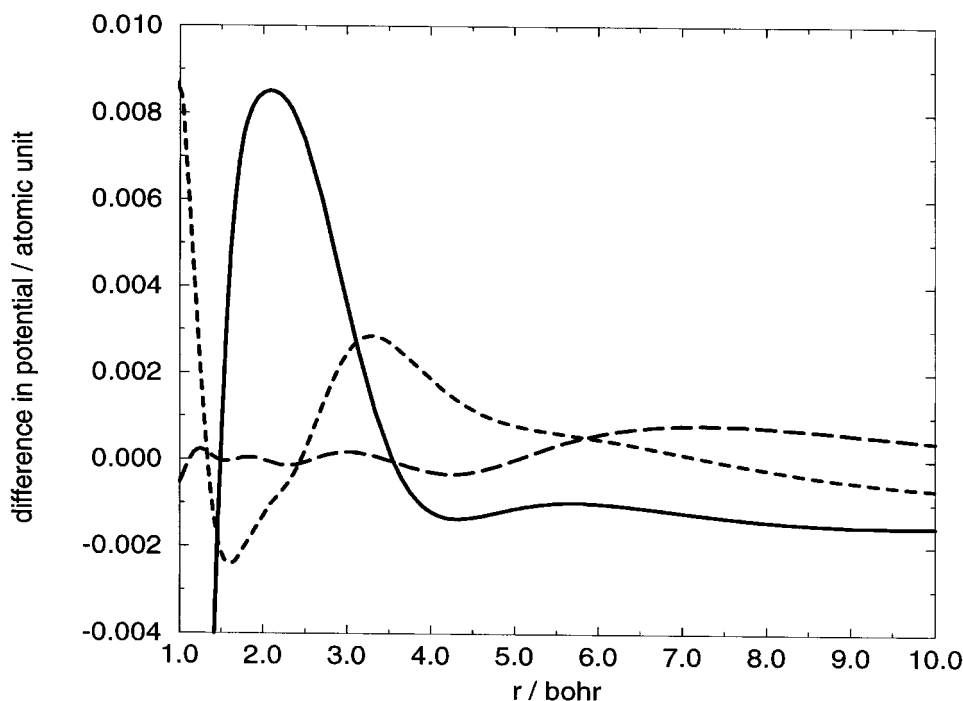


FIGURE 1. Difference between the Becke functional exchange potential with an exponential density and that calculated with various Gaussian approximations to the density for  $r$  close to the nucleus. (—) The STO-2G potential difference; (---) the STO-3G potential difference; and (- - -) the STO-6G potential difference.



**FIGURE 2.** Difference between the Becke functional exchange potential with an exponential density and that calculated with various Gaussian approximations to the density for  $r$  far from the nucleus. The curve designations are the same as in Figure 1.

### FUNCTIONAL GENERATOR HIERARCHY

A series of increasingly complex functional generators is listed in Table V. The exchange energy densities and potentials arising from some of these are discussed below.

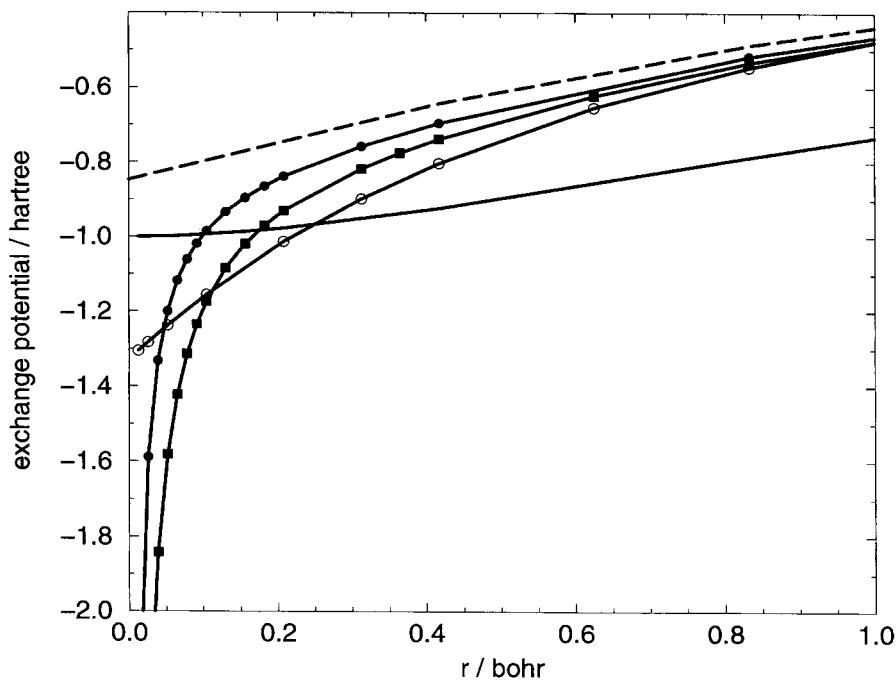
The potentials, evaluated as the functional derivative of the tabulated functionals generators for an exponential hydrogenic density together

with the exact potential, eq. (3), are plotted in Figure 3 for values of  $r$  close to the nucleus, and in Figure 4 for values of  $r$  in the asymptotic tail region of the density.

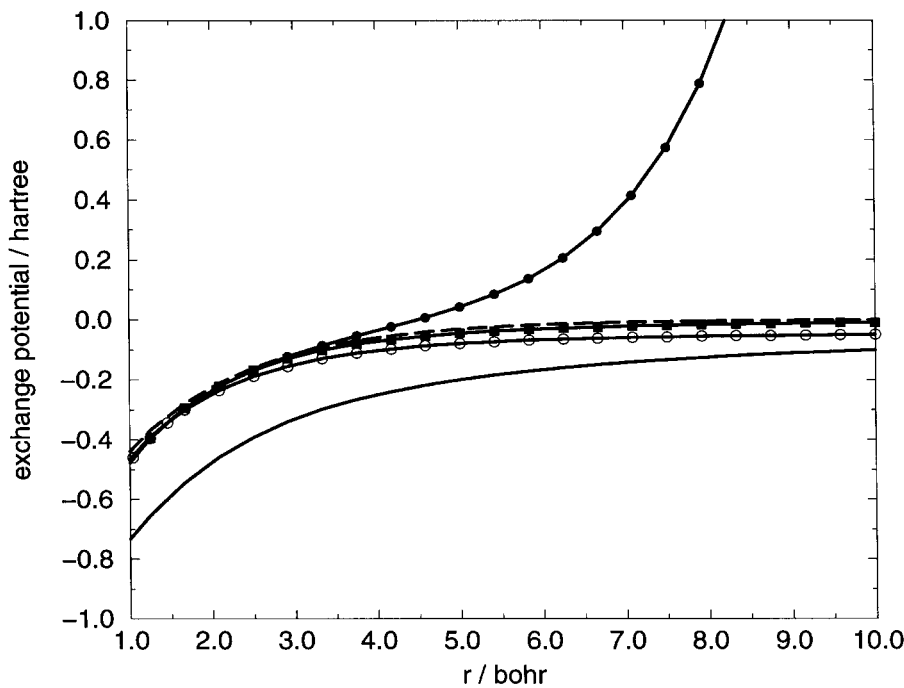
It can be seen that the different potentials show a very variable degree of success in recreating the true exchange potential for hydrogen, and this is reflected in their even greater variability in molec-

**TABLE V.**  
**Features of Exchange Potential for Various Functionals.**

	Functional			
	Dirac	Sham	Becke	xy
Designation	Local density	Almost homogeneous	First gradient correction	Second gradient correction
Reference	10	11	4	5
Formulation	$-C_x$	$-C_x - g_s$	$-C_x - g_B(\beta)$	$-C_x - g_B(\gamma)g_{xy}$
	$C_x = \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3}$	$g_s = \frac{7}{144} (81\pi^5)^{-1/2} x^2$	$g_B(\beta) = \beta x^2 [1 + 6\beta x \operatorname{arcsinh}(x)]^{-1}$	$g_{xy} = \left[ 1 + \frac{2y}{x^2} \right]^{-1}$
Constants			$\beta = 0.0042$	$\gamma = 0.0586$
$\lim_{r \rightarrow 0} (v_x)$	-0.85	$-0.020/r$	$-0.040/r$	-1.2
$\lim_{r \rightarrow \infty} (v_x)$	$-0.85 \exp(-2r/3)$	$0.0065 \exp(2r/3)$	$-1.25/r^2$	$-1.0/r$



**FIGURE 3.** Exchange potential obtained from the functionals in Table V for  $r$  close to the nucleus. (—) The exact potential; (---) the local density approximation potential; (●) the Sham potential; (■) the Becke potential; and (○) the  $xy$  potential.



**FIGURE 4.** Exchange potential obtained from the functionals in Table V, for values of  $r$  in the exponential tail of the density. The curve designations are the same as in Figure 3.

ular calculations. Both the Sham and Becke potentials diverge to  $-\infty$  as  $r$  tends to zero, and the local density approximation potential underestimates the exact potential value of  $-1$  at  $r = 0$ . As  $r$  becomes large, the local density potential decays exponentially to zero, while the Sham potential increases exponentially and the Becke potential decays as  $-\kappa r^{-2}$  (where  $\kappa = 5/4$  is determined by the hydrogen ionization potential), which is faster than the  $-r^{-1}$  behavior of the exact potential. The  $T(x, y)$  functional, first introduced in refs. 5 and 6, is included for comparison. This formulation can be seen to be the best representation close to the nucleus where it produces a value of  $-1.2$  for the potential and at long range, where it decays as  $-r^{-1}$ .

## Summary

A method has been devised to calculate symbolically, and for specific cases, the symbolic functional derivative of a functional of the electron density, its gradient, and Laplacian. This may easily be extended to include higher derivatives, and this method provides a useful tool for computations that are difficult and tedious to do by hand. This method has further been implemented in a freely available program.<sup>2</sup> It has been shown how this method can be used extensively in the investigations of different formulations for the exchange potential. The particular usefulness of this methodology is shown in the generation of a new formulation involving the Laplacian of the electron

density, which accurately reproduces the exact hydrogenic exchange energy density and potential at the nucleus and asymptotically, which gives the correct uniform electron gas limit.<sup>5</sup>

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